microporous filtration in place of or as an adjunct to rotary-vacuum filtration has great potential as a means of clarifying dextrose hydrolyzate and removing these particles.

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Preparation and Calcium Complexation of Oxidized Polysaccharides

Part I: Oxidation of Maltodextrins and Starch with Alkaline Sodium Hypochlorite

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The oxidation of maltodextrins and starch with aqueous alkaline sodium hypochloride has been studied. At an oxidant level of 3 moles hypochlorite per anhydroglucose unit at pH 8–9, a C2, C3-glycol-cleaved dicarboxy polysaccharide was obtained containing up to 45% ring-opened glucose units. Hydrolysis of the oxidation products yielded (apart from glucose) erythronic and glyoxylic acids, but no glucuronic acid evidencing the absence of C6-oxidation. The average degree of polymerization of the products ranged from 14 to 87 and indicated severe chain degradation during the oxidation. The products were shown to be effective calcium complexing agents and behaved as regular polyelectrolytes with identical complexing sites.

Darstellung und Calcium-Komplexierung von oxidierten Polysacchariden. Teil 1: Oxidation von Maltodextrinen und Stärke mit alkalischem Natriumhypochlorit. Die Oxidation von Maltodextrinen und Stärke mit wäßrigem alkalischem Natriumhypochlorit wurde untersucht. Bei einem Oxidantlevel von 3 Mol Hypochlorit je Anhydroglucoseeinheit bei pH 8–9 wurde an der C2, C3-Glykolbindung gespaltenes Dicarboxy-Polysaccharid erhalten, das bis zu 45% ringoffene Glucoseeinheiten enthielt. Die Hydrolyse der Oxidationsprodukte ergab neben Glucose, Erythron- und Glyoxylsäuren, jedoch keine Glucuronsäure, was auf nicht stattgefundene Oxidation am C6-Atom hinweist. Der durchschnittliche Polymerisationsgrad der Produkte lag zwischen 14 und 87 und wies auf starken Kettenabbau während der Oxidation hin. Es wurde gezeigt, daß die Produkte wirksame, Calcium komplexierende Agenzien sind und sich wie reguläre Polyelektrolyte mit identischen komplexierenden Stellen verhalten.

1 Introduction

The Oxidation of starch with aqueous alkaline sodium hypochlorite is an important industrial process for the preparation of so-called thin-boiling starches, with applications in the paper, textile and food industries. Oxidant levels of up to 60 g/kg starch (about 0.15 mole OCl^-/mole glucose units) are applied. The major effect of the oxidation is chain degradation, presumably *via* β-elimination in intermediate ketoglucose residues. In addition, carbonyl and carboxyl functions are introduced [1–7]. The starch largely remains in a granular form.

The application of higher oxidant levels (up to 4 moles OCl^-/glucose unit) yields fully dissolved starches with a higher carboxyl content. *Whistler* et al. [8, 9] reported that hypochlorite oxidations of amylose, amylopectin and methyl 4-O-methyl-α-D-glucopyranoside are not random. At pH 7–9 the major pathway is C2, C3-glycol-cleavage of glucose units, giving erythronic and glyoxylic acids after hydrolysis:

In contrast with this, *Boruch* [10] recently found gluconic and glucuronic acids as the only acidic fragments upon oxidation of starch, which would indicate oxidation exclusively at C1 and C6.

The mechanism of the hypochlorite oxidation of polysaccharides is uncertain, which is partly due to the complex nature of the oxidant in aqueous solution. The ratio $HOCl/OCl^-$ is pH dependent, HOCl being a weak acid ($pK_a = 7.54$ [11]). *Whistler* et al. [8, 12] proposed a heterolytic pathway with formation of a keto-group at C_2 or C_3 (*via* the hypochlorite ester) as the first step, followed by enolization, addition of HOCl and subsequent C–C cleavage (Fig. 1). Other authors found a second order dependence of the reaction rate on the hypochlorite concentration and assumed a homolytic pathway involving hydroxyl [13–16] or chloroxy radicals [17, 18]. Probably, both homolytic and heterolytic pathways are operative [19], the nature of which might be elucidated from studies with model alcohols.

Hypochlorite-oxidized polysaccharides, based both on starch [20] and cellulose [21, 22], have been recognized as potentially attractive phosphate substitutes in detergents owing to their good calcium complexing properties. This fact supports the C2, C3-glycol-cleavage mechanism since C2, C3-dicarboxy starch prepared by the well known two-step (periodate-chlorite)

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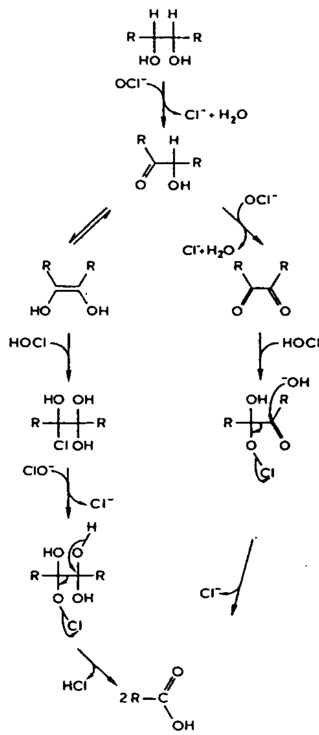

Fig. 1. Heterolytic pathway for glycol-cleavage by alkaline sodium hypochlorite as proposed by *Whistler* et al. [8].

oxidation is also a very effective Ca(II) complexant [23–25]. In this paper we report on the hypochlorite oxidation of maltodextrins and starch, applying 3 equivalents of oxidant per anhydroglucose unit at pH 7–9. The controversy in the literature concerning the selectivity of the oxidation induced us to examine the product composition by means of a reliable HPLC procedure [26]. The effect of added cobalt(II) and bromide, known to accelerate hypochlorite oxidations [14, 27–29] and to increase the carboxyl content of the products [27–29] at lower oxidant levels, was briefly explored. In addition, the Ca(II) complexing properties of the oxidation products have been evaluated and related to the theory of complexation by polyelectrolytes.

2 Experimental

2.1 Materials

Potato starch was obtained from Merck (Darmstadt, FRG). Amylose and maltodextrins (Paselli MD10, MD6 and SA2) were gifts from AVEBE (Veendam, The Netherlands). The maltodextrins were prepared by enzymatic hydrolysis of potato starch and are characterized by their dextrose equivalent (DE; % reducing end) from which their degree of polymerization DP is derived (DP = 100/DE) as a number average. Sodium hypochlorite solution (technical quality, about 15% active chlorine, 1.30–1.45 mmole OCl^-/g, pH 11.5) was obtained from OPG Pharma (Utrecht, The Netherlands). Dextrans of narrow molecular weight distribution were obtained from Serva (Heidelberg, FRG) (dextran FP70, $\bar{M}_n = 6.5-7.3 \cdot 10^4$; dextran FP40, $\bar{M}_n = 3.6-4.4 \cdot 10^4$; dextran 15, $\bar{M}_n = 1.5-2.0 \cdot 10^4$; dextran 4, $\bar{M}_n = 4-6 \cdot 10^3$). All other reagents were analytical-grade commercial products and were used without prior purification.

2.2 Oxidation

Maltodextrin or starch (10.0 g, 62 mmole anhydroglucose units) was dissolved or suspended in 100 ml water in a mechanically stirred glass reactor at 293 K in the dark. Sodium hypochlorite (133 g solution of 1.40 mmole/g; 186 mmole) of the appropriate pH (prepared from a pH 11.5 stock solution by the addition of 20% HCl) was added at once. The pH was kept constant by automatic addition of 2.50 M NaOH (Metrohm pH-stat). The reaction was followed by iodometric titration (oxidant consumption) and alkali consumption (formation of carboxyl groups). After complete (> 98%) oxidant consumption the reaction mixture was brought to pH 9, the product was precipitated by the dropwise addition (30 min) of two volumes 96% ethanol. The gummy precipitate was dissolved in 100 ml water, reprecipitated with 200 ml ethanol in order to decrease the NaCl content, dissolved in 20 ml water and freeze-dried to yield the dicarboxy oligo- or polysaccharide as a yellowish powder. The NaCl content was below 1% (ion-chromatography).

2.3 Determination of the carboxylic acid content of the oxidation products

0.5 g freeze-dried product was dissolved in 20 ml water, exchanged twice with excess of strongly acidic cation exchange resin (Dowex AG50-W-X8, H^+), and freeze-dried in order to remove the HCl (formed from the NaCl present in the oxidation product) which would interfere with the determination of COOH groups. This product was dissolved in 50 ml water and back-titrated with 0.1 M HCl after the addition of 1.00 ml 2.50 M NaOH to give the COONa content.

2.4 HPLC analysis of oxidation products

Freeze-dried product (60 mg) was dissolved in 0.5 M HCl (1 ml) and heated at 368 K for 10 h. The solution was brought to pH 9 by the addition of solid Na_2CO_3, filtered and analyzed by two HPLC methods. Method A (carboxylic acid components): column, Alltech BA-X8; eluent, 0.16 M NaCl + 0.02 M $MgCl_2$; 358 K; RI and UV_{212} detection [26].
Method B (non-carboxylic acid components): column, Biorad HPX-87-C (Ca(II) form, with mixed-bed guard column); eluent, H_2O; 333 K; RI detection.

2.5 Gel permeation chromatography

Freeze-dried product was dissolved (1.25 mg/ml) in a 0.1 M phosphate buffer (pH 7) and analyzed on a Biosil TSK-250 column with the same eluent, 293 K, RI and UV_{214} detection. The column was calibrated with dicarboxy dextrans of known molecular weight distribution (prepared by periodate-chlorite oxidation of dextran, assuming no degradation during the oxidation [30]) and with C2–C3-dicarboxy cellulose of $\bar{M}_w$ $5.2 \cdot 10^4$ (determined with light-scattering by the Zimm plot method [31]). $\bar{M}_w$ and $\bar{M}_n$ of the oxidation products were calculated by relating the area of two minute elution intervals to the average molecular weight of the interval determined from the calibration plot [32].

2.6 Calcium complexation

A Philips IS 561 Ca-ion-selective electrode, an HNU ISE-40-01-100 single junction reference electrode and a Metrohm 654 pH meter and 655 dosimat (automatic burette) were used. The automatic titration was controlled by a Spectra-Physics SP 4270 integrator. The data were processed with a Lotus-1,2,3 spreadsheet.
Calibration of the Ca-ion-selective electrode was performed using 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} M solutions of $CaCl_2$ buffered at pH 10 (NH_3) at ionic strength $\mu = 0.02$ (NaCl). Linear calibration plots were obtained up to 10^{-6} M, provided that douply distilled water and polyethylene storage bottles are used for the 10^{-5} and 10^{-6} M solutions.
To a solution of the complexant (0.1 g/100 ml water, pH 10.8 (NH_3), $\mu_0 = 0.02$, 61 mg NaCl, 298 K) was added 8 ml 0.1 M $CaCl_2$ solution at 2 min intervals (40 additions of 200 µl). The activity of uncomplexed Ca(II) was measured just before each subsequent addition.
For the calculation of the complexation constant as a function of the fraction associated Ca(II) complexing sites a Ca(II)/COO^- stoichiometry of 0.5 was assumed (*vide infra*). The molecular weight of a dicarboxy unit was corrected for the degree of oxidation of the dicarboxy polysaccharide. The dicarboxy unit molecular weight is

$\frac{1}{0.5 \cdot \text{COONa content}}$ (COONa content in mole/g).

3 Results and Discussion

3.1 Effect of pH

The NaOCl conversion plots (Fig. 2) of starch oxidations at pH 7–9 show the oxidant to be most rapidly converted at pH 7.0. This is in conformity with the results of other authors for the oxidation of amylopectin [8] and alginic acid [12] and, at lower oxidant levels, wheat and waxy maize starch [3], potato starch [27, 33, 34] and cotton cellulose [13, 14]. The maximum at pH 7 has been ascribed to a maximum at this pH of the function $[HOCl]^{1.5} [OCl^-]^{0.5}$, which was found to describe the rate of hypochlorite oxidation of cotton at pH 4–11 [14]. Also, the rate of self-decomposition of hypochlorite to chlorate and chloride is highest at pH 7 [35]. However, it should be noted that in heterogeneous starch systems the pH is always considerably higher in the solid phase (where the reaction takes place) than in solution, due to OH^- absorption into the granule [36]. At the high oxidant/substrate ratio used in this study, the starch remained granular until dissolution at about 40% oxidant conversion. Thus, an exact determination of the kinetics of these oxidations is practically impossible. For oxidation at pH 8.5 and 9 the ratio of consumed OH^- and OCl^- was constant (Fig. 3) indicating a constant selectively to carboxyl group generating reactions. However, at pH 7 and 8 the ratio OH^-/OCl^- increased with the conversion which suggests an initially greater tendency to reactions that do not form protons (e. g. formation of a ketone from a secondary hydroxyl group).

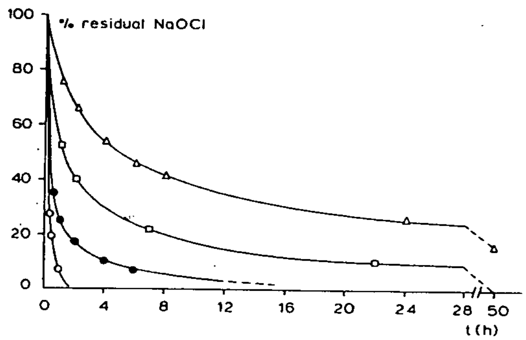

Fig. 2. Effect of pH on the hypochlorite conversion during starch oxidation. Starch (10 g, 62 mmole anhydroglucose units) in 100 ml water, sodium hypochlorite (186 mmole), pH 7–9, 293 K. pH 7.0 (○), pH 8.0 (●), pH 8.5 (□), pH 9.0 (△).

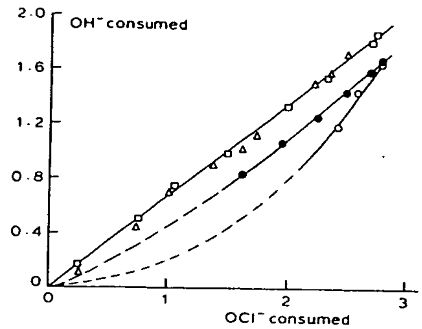

Fig. 3. Correlation between the alkali and hypochlorite consumption (expressed in mole/mole glucose units) during starch oxidation. pH 7.0 (○), pH 8.0 (●), pH 8.5 (□), pH 9.0 (△).

The yield and carboxyl content of the products were highest for oxidation at pH 8.5 (Table 1A). This is in accordance with previous results claiming maximum carboxyl content [4, 27] between pH 8 and 9.

The course of the oxidation (Fig. 4) was determined from HPLC analysis (Method A) of the oxidation products after their hydrolysis (0.5 M HCl, 368 K, 10 h) to monomeric fragments. Fig. 5A reveals erythronic and glyoxylic acids as the major acidic fragments from hydrolysis of the pH 8.5 product (1.98 and 1.80 mmole/g, respectively), indicative of C2, C3-glycol-cleavage as the predominant oxidation pathway [37]. Also, some glycolic, oxalic and formic acids are present (up to 0.50 mmole/g). Reducing end units are known to be oxidized by alkaline hypochlorite [15] but no gluconic acid was detected.

Table 1.
Dicarboxystarches Obtained from Oxidation with Sodium Hypochlorite[a]).

Entry	Substrate	pH	COONa content (mmole/g)	Yield[b]) (%)	SC (mmole/g)	log K_{int}	$\overline{M}_w \cdot 10^3$	$\overline{M}_n \cdot 10^3$	$\overline{DP}_n$
A. 1	starch	7.0	3.22	38	0.31	5.32	8.4	3.5	19
2	starch	8.0	4.51	44	0.77	5.92	35	13	67
3	starch	8.5	5.43	86	1.04	6.05	32	9.3	46
4	starch	9.0	5.33	78	1.05	6.23	30	9.4	47
B. 5	starch	8.5	5.43	86	1.04	6.05	32	9.3	46
6	starch[c])	8.5	5.20	73	0.83	5.93	19	5.1	25
7	starch[d])	8.5	5.57	47	1.08	6.04	[e])	[e])	[e])
C. 8	starch[f])	8.5	5.84	91	1.18	6.25	48	18	87
9	starch	8.5	5.43	86	1.04	6.05	32	9.3	46
10	DP 50	8.5	5.57	87	1.03	6.14	27	6.0	29
11	DP 16	8.5	5.51	85	0.91	5.95	22	5.2	26
12	DP 10	8.5	5.44	77	0.89	6.07	21	5.3	26
D. 13	prod. A.3[g])	8.5	6.81	38	1.77	6.37	14	3.0	14

[a]) Maltodextrin or starch (62 mmole anhydroglucose units) in 100 ml water, sodium hypochlorite solution (186 mmole), 293 K. [b]) Approximate yield, assuming all COONa originates from dicarboxy glucose units. [c]) $2 \cdot 10^{-2}$ mole % $CoCl_2$ and $8 \cdot 10^{-1}$ mole % NaBr (based on glucose units) added. [d]) $8 \cdot 10^{-1}$ mole % NaBr added. [e]) Not determined. [f]) Oxidation at 278 K. [g]) Reoxidation of dicarboxy starch A.3 with 3 mole hypochlorite per residual glucose unit (as estimated from the carboxyl content of A.3).

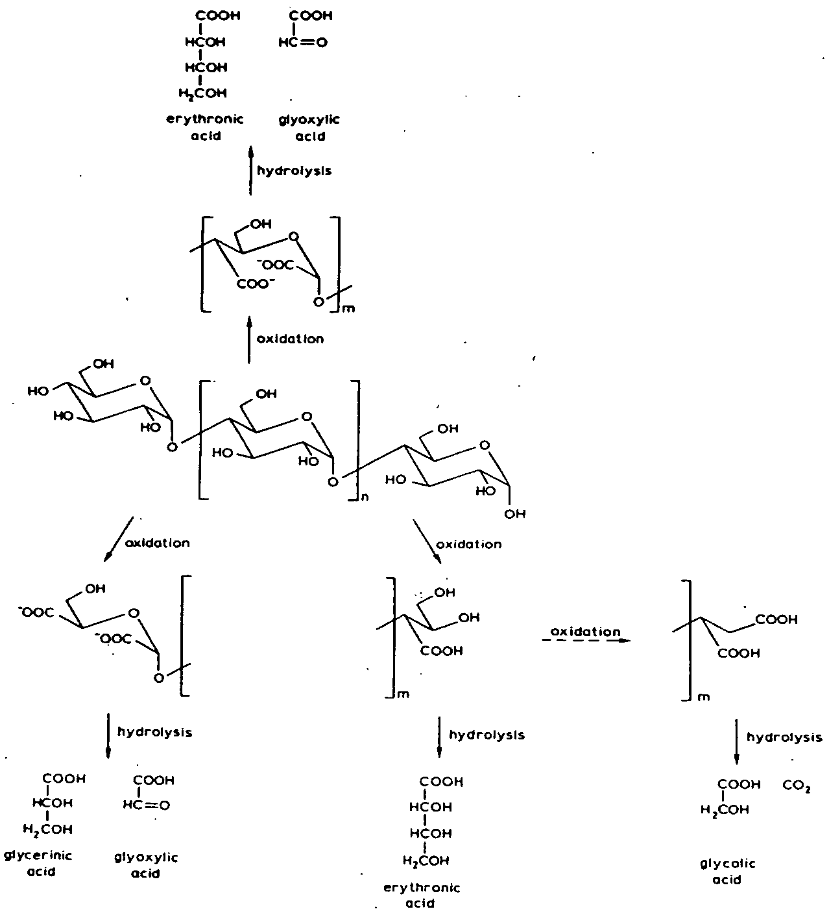

Fig. 4. Major pathways of starch oxidation (shown for non-reducing, reducing and internal glucose units) with sodium hypochlorite at pH 8–9.

Apparently, stepwise degradation occurred until the glycosidic bond is reached giving erythronic acid as the reducing end group. From the absence of glucuronic acid (eluting before erythronic acid) it can be concluded that no C_6-oxidation occurred in the alkaline pH range studied. This is in contrast with the recent conclusions from paper-chromatography of *Boruch* [10] but confirms the conclusion of *Whistler* et al. [8, 9]. The latter authors used a molar ratio of 2 hypochlorite per glucose unit and concluded that glycol-cleavage was the major reaction pathway, accounting for up to 27% oxidant use. The

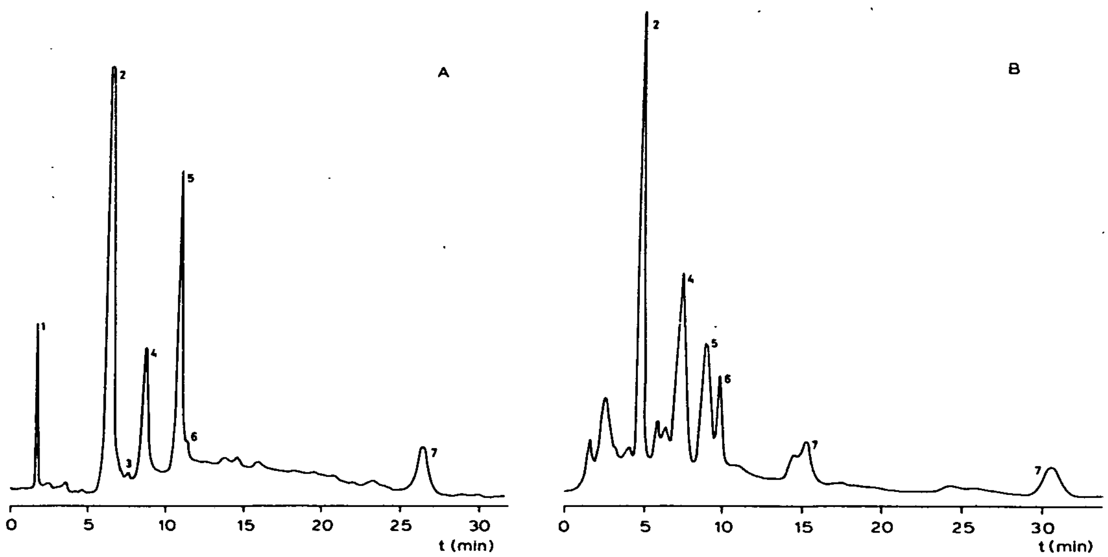

Fig. 5. HPLC analysis (Method A) of carboxylic acid products formed upon hydrolysis of dicarboxy starch.
A: pH 8.5, 293 K (Table 1, entry 3). B: pH 7.0, 293 K (Table 1, entry 1).

1. exclusion peak (inorganic acids and solvent) 2. erythronic acid 3. glycolic acid 4. oxalic acid 5. glyoxylic acid 6. formic acid 7. unknown component

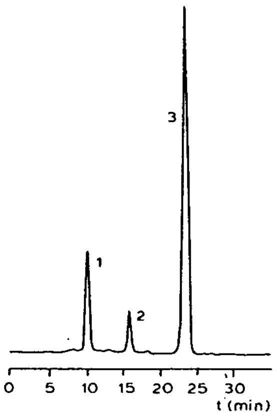

Fig. 6. HPLC analysis (Method B) of neutral products formed upon hydrolysis of dicarboxy starch. pH 8.5, 293 K, (Table 1, entry 3).

1. glucose
2. erythronolactone
3. sorbitol (internal standard)

remainder of the oxidant was consumed in oxidation of small fragments cleaved from the polymer chain giving about 0.6 CO_2/glucose unit. The oxidant was also converted into the oxidatively inactive chlorate (29% at pH 7, 5% at pH 9). According to our analysis 45% of the glucose units will be C2, C3-glycol-cleaved at pH 8–9. At pH 7, the efficiency and selectivity of the oxidation are markedly reduced giving only 1.04 mmole/g erythronic acid and 0.38 mmole/g glyoxylic acid (Fig. 5B). HPLC analysis (Method B; Fig. 6) of the non-carboxylic acid components showed only glucose as a hydrolysis fragment.

Hypochlorite oxidations are known to be strongly degradative [6, 39], presumably *via* β-elimination of intermediate keto-glucose units [40]. In order to determine the extent of degradation the molecular weights of the oxidation products were determined by gel permeation chromatography (Table 1). Indeed considerable depolymerization was observed, the number average molecular weight $\bar{M}_n$ ranged from $3.5 \cdot 10^3$ (oxidation at pH 7) to $13 \cdot 10^3$ (pH 8). The products are highly polydisperse, as is indicated by the high ratios of $\bar{M}_w/\bar{M}_n$.

3.2 Effect of additives

A drawback of the oxidation at pH 8.5 is the relatively slow consumption of the final 20% of oxidant. Hypochlorite oxidations are known to be accelerated by the addition of a cobalt(II) salt [14, 27–29]. Also, bromide ions might accelerate the reaction [1, 41, 42] through *in situ* conversion into hypobromite, which is a faster oxidant than hypochlorite. Comparison of the initial and 15 h rate of OCl^- conversion for the system without additive, with those in the presence of bromide and of cobalt + bromide (Table 2) shows that, at the concentrations applied, these additions exert no significant accelerating effect. In addition, enhanced chain degradation occurred in the presence of Co(II), as indicated by the lower $\bar{M}_w$ of the oxidation products (Table 1 B).

Table 2.
Hypochlorite Conversion Rates During Starch Oxidation[a]).

Entry	Rate[b]) t = 0 h	Rate[b]) t = 15 h
no catalyst (Table 1, entry 5)	2.1	$2.1 \cdot 10^{-2}$
Co(II) + Br^- (Table 1, entry 6)	2.4	$3.0 \cdot 10^{-2}$
Br^- (Table 1, entry 7)	2.1	$2.2 \cdot 10^{-2}$

[a]) 62 mmole starch in 100 ml water, 186 mmole hypochlorite solution, pH 8.5, 293 K. [b]) Expressed as mole OCl^-/h · mole glucose units.

3.3 Calcium complexation

The calcium complexing properties of the hypochlorite oxidized starches were evaluated by titration of a 100 ml solution of the complexant (100 mg) with a 0.1 M calcium chloride solution. The activity of uncomplexed Ca(II) was measured with a Ca(II)-ion-selective electrode. The calcium sequestering capacity SC is defined as the number of mmoles of Ca(II) that can be added to one gram complexant (at the above conditions) until the concentration of non-complexed Ca(II) reaches 10^{-5} M. This value is generally considered the upper limit for Ca(II) during the washing process [43]. The SC is a practical measure of the value of the complexant on a weight basis [44].

As expected from the increased selectivity to C2, C3-glycol-cleaved dicarboxy starch going from pH 7 to pH 8–9, the Ca(II) complexation was better for products prepared at as higher pH of oxidation (Fig. 7, Table 1 A). This also explains the better detergency found for the products oxidized at pH 8–9 [20].

The dependence of the SC on the molecular weight of the dicarboxy polysaccharides was studied with starch and the maltodextrins DP 50, DP 16 and DP 10 as substrates (Table 1 C). Starch oxidized at 278 K instead of 293 K was also included since this procedure gave a product with a relatively high chain length. Fig. 8 clearly shows that a higher molecular weight improves the SC (corrected for the slightly different COONa

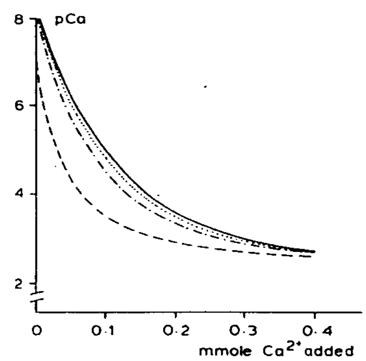

Fig. 7. Calcium-ion-selective electrode titration curves of starch oxidation products (0.1 g/100 ml water, pH 10.8, $\mu = 0.02$, 298 K). Effect of pH of hypochlorite oxidation.

pH 7.0 (– – –); pH 8.0 (– · –); pH 8.5 (· · ·); pH 9.0 (—)

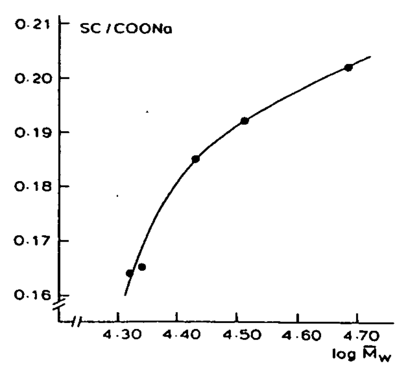

Fig. 8. Dependence of the sequestering capacity (corrected for the carboxyl content) on the molecular weight of oxidized starch and maltodextrins (Table 1, entries 8–12).

content of the products). The degradative effect of added Co(II) is reflected by the low SC of the product (Table 1, entry 6). At our laboratory, *Nieuwenhuizen* et al. [23] recognized the dependence of the Ca(II) complexation constant on the molecular weight for periodate-chlorite glycol-cleaved dicarboxy polysaccharides. Formation of a helix structure, creating effective complexing sites between non-neighbouring dicarboxy units, was tentatively proposed. The positive effect of a higher chain length on the Ca(II) complexation of hypochlorite-oxidized starches also suggests cooperation of sites. Helix formation, however, is considered rather improbable because of the relatively low abundance of dicarboxy units (about 45%) [45].

When dicarboxy starch was subjected to a second hypochloride oxidation, the product showed a sharply increased SC, in spite of a further reduction of the $\bar{M}_w$ (Table 1, entry 13). The 25% increased carboxyl content, from about 45 to 65% dicarboxy units, gave a 70% increase in sequestering capacity. Apparently, above a critical value of the carboxyl content, more effective Ca(II) complexing sites are created. At a low carboxyl group density steric hindrance between non-carboxyl chain segments will prevent formation of effective complexing sites. From ^{17}O NMR studies with periodate-chlorite glycol-cleaved starch and β-cyclodextrin, using Dy(III) as a model ion for Ca(II), it was concluded that such sites may involve up to 8 ligand oxygen atoms (carboxylate, acetal and possibly also CH_2OH groups) [23, 46]. A similar sharp increase in the SC (going from 40 to 60% dicarboxy units) has been found for dicarboxy starches obtained by the periodate-chlorite method [46].

Since calcium complexation by a polyelectrolyte involves many complexing sites no „single" complexation constant can be derived. However, if the sites are assumed to be identical and completely independent, the individual complexation constants for each site can be statistically transformed into [31]:

$$\frac{Z}{1-Z} = K \cdot [Ca]$$

where Z is the metal-ion-coordinated fraction of the polymer sites and $1-Z$ is the fraction of non-coordinated sites. For the dicarboxy polysaccharides, interaction between the sites cannot be neglected. An intrinsic complexation constant K_{int} is now defined for $Z = 0$. The standard free energy for this situation is ΔG^0_{int}. For polyelectrolytes where interactions are predominantly electrostatic in nature, it can be shown that ΔG^0_{int} should change upon complexation according to a linear function of Z [31]. The complexation constant then becomes:

$$K = \frac{Z}{[Ca](1-Z)} = K_{int}\, e^{cZ}$$

or, converted to logarithmic form (with $a = c \cdot \log e$):

$$pCa + \log \frac{Z}{1-Z} = aZ + \log K_{int}$$

Fig. 9 shows the Ca(II) complexation data for the hypochlorite-oxidized starches when $pCa + \log (Z/(1-Z))$ is plotted as a function of the fraction of combined sites Z. For calculation of Z (see Experimental) the complex stoichiometry was assumed to be 1 Ca(II)/2 COO^-, as is indicated by the *Job*'s plot [47] given in Fig. 10. In accordance with the theory, the curves are linear (up to $Z = 0.65$) with slope a and Y-intercept log K_{int} (Table 1), indicating a regular structure with identical com-

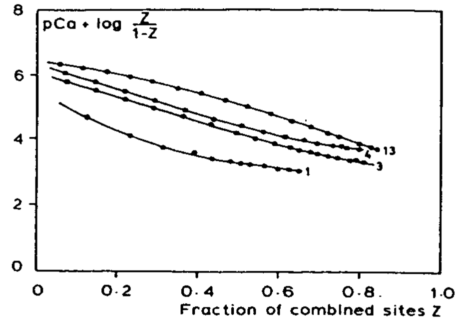

Fig. 9. Dependence of the complexation constant on the fraction of combined Ca(II)-complexing sites Z. Numbers refer to the entries of Table 1.

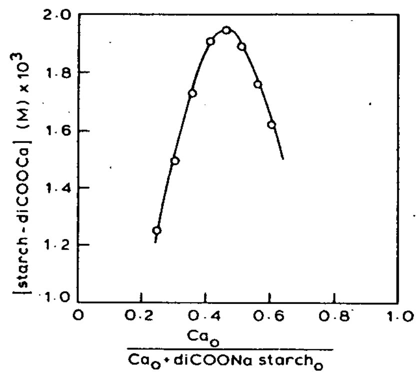

Fig. 10. *Job*'s plot for dicarboxystarch (Table 1, entry 3). Solutions of dicarboxystarch (5 mM dicarboxy units, pH 10.8, $\mu = 0.02$) and $CaCl_2$ (5 mM) were mixed at different ratios. The concentration of the complex was determined from the concentration of uncomplexed Ca(II) measured with a Ca-ion-selective electrode (298 K).

plexing sites. The negative slopes reflect a decreasing affinity of the polymer upon complexation for additional Ca(II) ions which is, of course, expected for the decreasing electrostatic interaction between the polyelectrolyte and the Ca(II) ions. At high degrees of association ($Z > 0.75$) the polymers start to precipitate which complicates the titration. The pH 7 oxidized product shows a nonlinear behaviour as might be expected from the aselective oxidation and the severe degradation at this pH. On the average, K_{int} correlates linearly with the SC (Fig. 11). The substantial individual deviations, due to different slopes a, are related to differences in chain length and in conversion and selectivity of the oxidation.

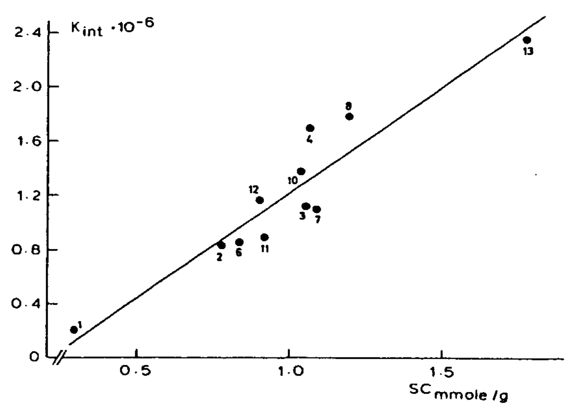

Fig. 11. Correlation between K_{int} and the sequestering capacity. Numbers refer to the entries of Table 1.

As to the applicability of the dicarboxy starches as a detergent (co-)builder it should be noted that a pK_{int} larger than 5 at $Z = 0.4-0.5$ is a prerequisite [48]. The starches oxidized at 8.5–9 meet this specification. From a practical point of view, the oxidation is preferentially performed at pH 8.5 because these conditions combine a reasonable reaction time with good selectivity, yield and Ca(II) complexing properties.

4 Conclusions

- C2, C3-glycol-cleaved dicarboxy polysaccharides (up to 45% dicarboxy glucose units) are obtained from oxidation of maltodextrins and starch with sodium hypochlorite applying a molar ratio of 3 OCl^-/glucose unit at pH 8–9.
- The products show good calcium complexing properties (log K_{int} up to 6.25, sequestering capacity 1.18 mmole/g) and behave as regular polyelectrolytes with identical complexing sites.

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[36] The addition of 0.10 mmole OH^- to 10 g starch in 100 ml water gives pH 8 instead of 11 indicating approximately quantitative OH^- absorption into the granule under these circumstances.
[37] It should be noted that the chromatograms sometimes show additional peaks at about 26 and 31 min. These can be ascribed to di- or tricarboxylic acids expected to elute at these retention times (e.g. partially hydrolyzed erythronic-glyoxylic acid structures or oligomers [38] of glyoxylic acid. As chromatograms virtually free of these peaks could be obtained in all relevant cases, no systematic study been performed as yet to prevent their formation.
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[44] Obviously, the fraction of sequestered Ca(II) is given by the difference of added and uncomplexed Ca(II) ions. At pCa = 5, however, the fraction of uncomplexed Ca(II) is only 1.1% (for product 3, Table 1).
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